FORM-U.S. PATENT & TRADEMARK OFFICE (Rev. 10-96) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: 000500-128

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5): Unassigned 09/101341

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/SE96/01698	18 December 1996	10 January 1996

TITLE OF INVENTION
A METHOD OF PRODUCING AN ABSORBENT MATERIAL, AN ABSORBENT MATERIAL AND ABSORBENT ARTICLES INCLUDING THE MATERIAL IN QUESTION

APPLICANT(S) FOR DO/EO/US
Kent MALMGREN and Bengt WIDBERG

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).
4. [X] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [X] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US)
6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.
14. [ ] A substitute specification.
15. [ ] A change of power of attorney and/or address letter.
16. [X] Other items or information:
    INTERNATIONAL SEARCH REPORT; PCT FORM IPEA/416; AND INTERNATIONAL PRELIMINARY EXAMINATION REPORT.

U.S. APPLICATION NO. (If known, see 37 C F.R. 1.50)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
Unassigned	PCT/SE96/01696	000500-128

17. ☒ The following fees are submitted:	CALCULATIONS	U S PATENT & TRADEMARK OFFICE USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)):		
Search Report has been prepared by the EPO or JPO $930		
International preliminary examination fee paid to USPTO (37 CFR 1.482) $720.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $790.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1070.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $98.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 1,070.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	15 -20 =	0	X$22.00	$ 0	
Independent Claims	1 -3 =	0	X$82.00	$ 0	
Multiple dependent claim(s) (if applicable)			+$270.00	$	
TOTAL OF ABOVE CALCULATIONS =				$ 1,070.00	
Reduction for ½ for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	-
SUBTOTAL =				$ 1,070.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$	
TOTAL NATIONAL FEE =				$ 1,070.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$ 40.00	
TOTAL FEES ENCLOSED =				$ 1,110.00	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of $ 1,110.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 02-4800 in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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30,888
REGISTRATION NUMBER

July 8, 1998

(10/97)

Patent
Attorney's Docket No. 000500-128

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of	)	
	)	
Kent MALMGREN et al.	)	Group Art Unit: Unassigned
	)	
Application No.: Unassigned	)	Examiner: Unassigned
	)	
Filed: July 8, 1998	)	
	)	
For: A METHOD OF PRODUCING AN ABSORBENT MATERIAL, AN ABSORBENT...QUESTION	)	

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified patent application please amend the application as follows:

IN THE CLAIMS:

The following amendments refer to the claims received in the International Application on March 25, 1998.

Please amend claims 3, 5, 7, 10, 11, 12, 13, and 15 as follows:

Claim 3, line 1, delete "or Claim 2".

Claim 5, lines 1 and 2, change "any one of the preceding Claims" to --Claim 1--.

Claim 7, lines 1 and 2, change "any one of Claims 1-4" to --Claim 1--.

Claim 10, lines 1 and 2, change "any one of Claims 7-9" to --Claim 7--.

Claim 11, lines 1 and 2, change "any one of the preceding Claims" to --Claim 1--.

Claim 12, lines 1 and 2, change "any one of the preceding Claims" to --Claim 1--.

Claim 13, line 2, change "any one of the preceding Claims" to --Claim 1--.

Claim 15, lines 3 and 4, change "any one of Claims 1-12" to --Claim 1--.

REMARKS

In the event that there are any questions concerning this amendment, or the application in general, the Examiner is

respectfully urged to telephone the undersigned attorney so that prosecution of the application may be expedited.

Respectfully submitted,

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WO 97/25463 PCT/SE96/01698

A METHOD OF PRODUCING AN ABSORBENT MATERIAL, AN ABSORBENT MATERIAL AND ABSORBENT ARTICLES INCLUDING THE MATERIAL IN QUESTION

TECHNICAL FIELD

The present invention relates to a method of producing polysaccharide fibre, the polysaccharide fibre thus produced and an absorbent article which includes polysaccharide fibres.

BACKGROUND OF THE INVENTION

Superabsorbents, that is to say absorbent material which is capable of absorbing several times, normally more than ten times, its own weight of water or body fluid, is used in absorbent articles, such as diapers, incontinence guards and sanitary napkins, to enhance the absorbency of the absorbent body of the article and also retention capacity, the remainder of the absorbent body normally consisting of cellulose fibres, so-called fluff pulp.

Polyacrylic acid is the polymer most used as superabsorbent non-renewable base. Polyacrylic acid is produced from oil. Since crude oil is a natural resource that is non-renewable, the use of oil as a starting material in the manufacture of polyacrylic acid creates a problem from an environmental aspect.

With the intention of resolving this problem, endeavours have been made to produce superabsorbents on the basis of renewable primary materials. These primary materials have included the different polysaccharides, such as starch and cellulose.

One polymer that has been used to a great extent in this context is carboxymethyl cellulose. This is a cellulose derivative with carboxymethyl as a substituent. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS. Carboxymethyl cellulose is relatively cheap and has high affinity to water-based liquids.

However, the admixture of carboxymethyl cellulose in absorbent articles such as diapers, incontinence guards and sanitary napkins is associated with serious drawbacks. When the article is wetted during use, the carboxymethyl cellulose will dissolve and therewith increase the viscosity of the liquid discharged by the wearer. This dramatically reduces the liquid dispersion rate. So-called gel blocking occurs. Carboxymethyl cellulose that has a degree of substitution below 0.35 is not soluble in water and could therefore be used favourably in absorbent articles with regard to the aspect of gel blocking. However, carboxymethyl cellulose that has a degree of substitution below 0.35 has poor absorption properties in comparison with polyacrylates. In other words, the carboxymethyl cellulose must have a degree of substitution greater than 0.35 in order to have good absorption properties, although such carboxymethyl cellulose is soluble in water and therewith presents a gel blocking problem.

Another drawback with the superabsorbents that are commercially available at present is the administration form. The superabsorbent is normally added to the article in which it shall be included in the form of grains, flakes or granules. A special metering apparatus is required to add superabsorbent in this form, and it is difficult to obtain uniform distribution of superabsorbent in the fibrous pulp body.

Superabsorbent in fibre form would be easier to meter. Because the absorbent body into which the superabsorbent is to be administered normally consists of fibres, there is a danger of superabsorbent particles separating-out from the fibre matrix. This

problem is alleviated with superabsorbents in fibre form. Although polyacrylate fibres are commercially available, they have not been used to any great extent. This is probably due to their high price and poor swellability.

A number of attempts have been made to produce polysaccharide fibres for use in sanitary products. WO 93/12275 discloses solvent spinning of polysaccharide fibre. However, the swelling properties of polysaccharide fibres produced in accordance with known techniques is too poor for such fibres to be of interest as a substitute for conventional superabsorbent material.

OBJECT OF THE INVENTION

An object of the present invention is to provide a superabsorbent material which is based on renewable primary material and which has an acceptable performance capacity in comparison with conventional superabsorbent materials.

Another object of the invention is to produce a superabsorbent material in an administration form which facilitates uniform metering of the superabsorbent material to a pulp body.

SUMMARY OF THE INVENTION

A method for producing a polysaccharide fibre of the kind mentioned in the introduction and having properties which enable the aforesaid problems associated with conventional superabsorbent material to be avoided is characterized in accordance with the invention by dissolving the polysaccharide in a solvent, extruding the solution down into a bath which includes a water-miscible organic solvent, preferably an alcohol, such as methanol, ethanol or isopropanol, or a ketone, such as acetone, and a cross-linking agent, such as a polyelectrolyte or a metal salt,

preferably a salt of a divalent, trivalent or quadrivalent ion, such as calcium, magnesium, iron, aluminium or zirconium.

DESCRIPTION OF THE INVENTION

Those polysaccharides that can be used to produce a polysaccharide fibre in accordance with the invention are, for instance, carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum, alginate.

As before mentioned, carboxymethyl cellulose, which is a cellulose derivative, is particularly well-suited for this purpose. The properties of the polymer are contingent on the degree of polymerization, DP, and the degree of substitution, DS.

The degree of polymerization, DP, denotes the number of monomer units in the polymer chain that influence the viscosity of an aqueous solution of the polymer.

The degree of substitution, DS, denotes the mean number of carboxymethyl substituents in the polymer chain. The degree of substitution influences the swelling properties of the polymer, and a degree of substitution above 0.35 gives a water-soluble polymer.

As before mentioned, a degree of substitution above 0.35 is desirable in order to obtain a high absorbency. However, this would result in a water-soluble polymer and therewith create gel-blocking problems.

Consequently, it would be desirable to produce a polysaccharide, for example, a carboxymethyl cellulose, that had a degree of substitution greater than 0.35 and which did not dissolve in water. This object is realized in accordance with the invention, by cross-linking the polymer. This cross-linking may be covalent or ionic.

The use of conventional cross-linkers to cross-link the polymer, such as epichlorhydrin and formaldehyde, would cause the coagulate to precipitate very slowly and fasten to the extrusion nozzle, therewith creating serious disturbances in a large-scale process.

According to the invention, the polymer is ionically cross-linked with the aid of polyelectrolytes or polyvalent metal ions, especially calcium, zirconium, aluminium or iron(III). When carboxymethyl cellulose is to be cross-linked, it is probable that cross-linking is effected by the formation of bonds between the carboxyl groups. Cross-linkers in the form of salts give fibres that are easily spun. The salt in which the polyvalent metal ion or the polyelectrolyte is present shall be soluble in water. The counter-ion to the metal ion or the polyelectrolyte, in other words the anion, is selected accordingly. Chloride is a suitable anion in this respect.

The cross-linked superabsorbent is then distributed in an absorbent body, which is normally comprised of cellulose pulp. The pulp may be in reels, bales or sheets which are dry-defibrated and converted into a fluffed state to form a pulp mat. As before mentioned, the material in the absorbent body may be cellulose fibres. Examples of other fibres conceivable in this regard are cotton fibres and synthetic fibres. It is also known to use foamed material in the absorbent body.

The problem of administering a superabsorbent in grain, flake or granule form evenly in the absorbent body is solved in accordance with the invention by choosing another administering form, namely a fibre form.

These fibres are produced in accordance with the invention by solvent spinning. Solvent spinning is carried out by pumping a polymer solution to a spinning nozzle, and extruding the solution into a bath containing a water-miscible organic solvent,

such as an alcohol. This solvent causes the polymer to precipitate in the form of fibres.

The extrusion bath may also contain water. The volume of water in the extrusion bath is determined by the fact that a given lowest organic solvent content is required to obtain good quality fibres. The lowest organic solvent content is about 70 vol%. The extrusion bath may thus contain about 0-30 vol% water.

As the polysaccharide which was earlier dissolved in water precipitates in the extrusion bath, the bath will become enriched with water. For the above-said reason, this water must be removed continuously to prevent the organic solvent content falling beneath about 70 vol%. The extrusion bath also includes one or more cross-linking agents in addition to the organic solvent. This method results in the simultaneous forming of fibres and cross-linking of the polymer.

The fibres are reeled-up from the extrusion bath, and dried and cut into appropriate lengths. An appropriate fibre length is 2-20 mm, preferably 4-8 mm. After this has been done, the fibres can be admixed in absorbent bodies intended for use in absorbent articles, such as diapers, incontinence guards and sanitary napkins.

According to one alternative embodiment of the invention, the fibres may also be subjected to post-treatment, in which the fibres are cross-linked covalently. Surprisingly, this covalent cross-linking of the fibres has been found to greatly increase the capillary liquid-retaining capacity of the fibres.

The following explanation as to why the covalent cross-linking enhances the liquid-retaining capacity of the fibres shall be seen solely as an hypothesis of how the invention can be assumed to function. The described hypothesis, or theory, shall not be considered as limiting the scope of the invention, but shall be seen solely as a

conceivable model of the manner in which the invention works, with the intention of facilitating an understanding of the invention.

The reason why the covalently bonded fibres have a surprisingly good retention ability may be because the covalently cross-linked fibres swell rapidly and copiously. The risk of gel-blocking decreases; a fibre network containing the covalently cross-linked fibres has very large pores in a swollen state. The fibres expand quickly and copiously, particularly longitudinally, which favours the expansion on the network in which the covalently cross-linked fibres are mixed and thereby enhances dispersion of liquid, or fluid, in the network.

This covalent surface cross-linking of the fibres can be achieved with various conventional cross-linkers, for example: 2,4,6-trichloro-1,3,5-triazine, epichlorohydrin, bis(epoxypropyl) ether, dichloroethane, divinylsulfone, ethylene glycol-bis(epoxypropyl) ether, formaldehyde, vinyl cyclohexane dioxide, 1,3-dichloro-2-propanol, 1,3-bis(β-hydroxy-t.-chlorpropoxy)-2-propanol, 1,3-bis(β-hydroxy-t.-chloropropoxy) ethane, 1,2:3,4-diepoxybutane, 1,1:5,6-diepoxyhexane, 2,3-dibromo-1-propanol, 2,3-dichloro-1-propanol, 2,2-dichloroethyl ether, methyl bis(acrylamide), N,N'-dimethylol(methylbis(acrylamide)), trisacrylol hexahydro-triazin, acrylamidemethyl chloroacetamide, 2,4,6-trichloropyrimidine, 2,4,5,6-tetrachloropyrimidine, cyanuric chloride, triallyl cyanurate, dichloroacetic acid, phosphorus oxychloride, bis(acrylamido) acetic acid.

These cross-linkers and cross-linking methods using these cross-linkers are described by Dean, Ferguson and Holst in the book "Absorbency", edited by P.K. Chatterjee, Elsevier Science Publishing Company, 1985.

In accordance with the invention, polysaccharide fibres may be produced by moulding (casting) as an alternative to extrusion. The polysaccharide fibres are

sprayed into a bath which contains solvent and one or more cross-linkers as described above, both when extruding and casting the fibres. However, when casting the fibres the solution is not sprayed through a nozzle as in the case with extrusion, but is instead sprayed onto a plate rotating in the bath.

The polysaccharide fibres produced in accordance with the invention can now be used as conventional superabsorbents, in other words can be mixed with fluff pulp or applied in layers between fluff pulp or between tissue layers. They can also be combined with other superabsorbents.

It will be understood that the invention is not restricted to the combinations described here, but that all combinations of solvents, cross-linkers and polysaccharides are included in the inventive concept.

Embodiments

Example 1 - Spinning of CMC-fibres having different aluminium contents

Equipment

Rayon spinning laboratory equipment was used, this equipment being shown in Figure 1.

The equipment comprised:

A pressure chamber, shown in detail in Figure 2.

A gear pump.

A spinning nozzle.

A rectangular plexiglass tank measuring 890x195x190 mm, to be used as an extrusion bath.

A beaker 10 containing a de-aerated carboxymethyl cellulose (CMC) solution 1 was placed in a pressure chamber 2. A lead weight 11 was placed on top of the solution. The chamber 2 was sealed and air having a pressure of 7.5 bars forced the CMC-solution through a steel pipe 12 and via a gear pump 4 to the spinning nozzle 3. The lead weight 11 prevented air from entering between the CMC-solution 1 and the steel pipe 12. The spinning nozzle 3 contained 20 holes 5, each having a diameter of 200 µm.

The CMC-solution 1 was extruded out into the extrusion bath 7 through the spinning nozzle 3. The extrusion bath 7 contained ethanol and aluminium chloride.

CMC-fibres 8 were drawn through the extrusion bath with the aid of a variable speed roller 9 driven by an electric motor. The CMC-fibres were held beneath the surface of the extrusion bath with the aid of a glass rod.

The fibres were then washed in ethanol (95%), being held for two minutes in the alcohol. This procedure was repeated two times. The washed fibres were dried at room temperature and then cut into lengths of 6 mm.

<u>A method of preparing the carboxymethyl cellulose solution</u>

Different concentrations of CMC were tested: 8% Cekol 10000 and 7% Cekol 50000 from Metsä-Särla Oy. Cekol 10000 and Cekol 50000 had mutually the same DS (0.6-0.9) but Cekol 50000 had a higher DP than Cekol 10000.

CMC in granule or powder form was mixed with water. The mixture was stirred (agitated) manually and the mixture then allowed to stand in a closed container for at least two calendar days.

The mixture was centrifuged and evacuated alternately, until all air bubbles in the mixture had disappeared. 600 g of the CMC-solution were placed in a plastic beaker (800 ml), the beaker being subjected to a vacuum for thirty minutes in order to remove air bubbles from the solution.

The extrusion bath

The extrusion bath had a volume of 8 l. Originally, it consisted of 95 vol% ethanol and 5 vol% water. Aluminium chloride was then added to the bath. The amount of aluminium chloride in the bath varied as shown in Figures 3 and 4. The concentration of aluminium chloride fell during the process, as the fibres absorbed the salt. It was therefore necessary to add aluminium chloride during the spinning process. The concentration of aluminium chloride was never allowed to fall by more than 10% during the process.

The aluminium content of the fibres

CMC-fibres were produced with different aluminium contents, by varying the aluminium content of the extrusion bath. Figure 3 shows the result obtained when using Cekol 10000 as the starting material, while Figure 4 shows the result obtained when using Cekol 50000 as the starting material.

Example 2 - Producing CMC-fibres with different baths

With the intention of discovering whether or not fibres could be formed in extrusion baths of mutually different compositions, tests were carried out with aluminium salts, iron salts, zirconium salts and magnesium salts in a bath with different solvents. The

CMC used was Cekol 50000. The solvents tested were ethanol, methanol, isopropanol and acetone. The following bath compositions were tested:

Metal salt	Liquid salt
1. 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% ethanol + 5 vol-% water
2 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% methanol + 5 vol-% water
3. 4.4 g $AlCl_3$-$6H_2O$/litre solution	85 vol-% acetone + 15 vol-% water
4. 4.4 g $AlCl_3$-$6H_2O$/litre solution	95 vol-% isopropanol + 5 vol-% water
5. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% ethanol + 5 vol-% water
6. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% methanol + 5 vol-% water
7. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% acetone + 5 vol-% water
8. 5.3 g $FeCl_3$-$6H_20$/litre solution	95 vol-% acetone + 5 vol-% water
9. 6.0 g $ZrCl_4$/liter solution	95 vol-% ethanol + 5 vol-% water
10. 6.0 g $ZrCl_4$/liter solution	95 vol-% methanol + 5 vol-% water
11. 6.0 g $ZrCl_4$/liter solution	95 vol-% isopropanol + 5 vol-% water
12. 15.5 g $MgCl_2$-$6H_2O$/liter solution	95 vol-% ethanol + 5 vol-% water
13. 15.5 g $MgCl_2$-$6H_2O$/liter solution	95 vol-% methanol + 5 vol-% water
14 15.5 g $MgCl_2$-$6H_2O$/liter solution	78 vol-% acetone + 22 vol-% water
15. 15.5 g $MgCl_2$-$6H_2O$/liter solution	90 vol-% isopropanol +10 vol-% water

Results

Fibres were obtained with all extrusion bath compositions.

Example 3 - Polyelelectrolytes as cross-linkers

CMC-fibres were produced from Cekol 50000 in accordance with the invention, there being used a spinning bath containing polyelectrolytes dissolved in 80 vol% ethanol and 20 vol% water. The compositions of the different spinning baths are described below.

Polyelectrolyte	Trade name	Content (weight %)
Polyvinyl amine	Basocoll (BASF)	0.05
Polybrene (quaternary polyamine)	Polybrene (Aldrich)	0.1

Result

Fibres could be produced in both baths.

Example 4 - Producing fibres from different types of polysaccharides

Concentrated aqueous solutions were produced from the following polysaccharides.

Polysaccharide	Trade name (manufacturer)	Concentration (weight %)
CMC	Cekol 2000 (Metsä-Serla OY)	12
CMC	Cekol 4000 (Metsä-Serla OY)	10
CMC	Cekol 10000 (Metsä-Serla OY)	8
CMC	Cekol 30000 (Metsä-Serla OY)	7.5
CMC	Cekol 50000 (Metsä-Serla OY)	7
Guar gum	Meypro® Guar (Meyhall)	10
Bean gum	Meypro® LBG (Meyhall)	10
Pectin	Genu® pectin type X-0905 (Copenhagen Pectin)	5

The solutions were then used to produce fibres in accordance with the invention, in a spinning bath consisting of 8 g $AlCl_3$ $6H_2O$/l in 95 vol% ethanol and 5 vol% water.

Result

Fibres could be produced from all of these polysaccharides.

Example 5 - Covalent cross-bonding of spun CMC-fibres

CMC-fibres produced from Cekol 50000 in accordance with Example 1 by spinning in a bath containing 3 g $AlCl_3$ $6H_2O$/l in 95 vol% ethanol and 5 vol% water were used in this test. 5 g of fibres cut to a length of 6 mm were placed in a glass beaker

containing 250 ml of distilled water and allowed to swell for about one minute. 250 ml of a 2 percent by weight solution of 2,4,6-trichloro-1,3,5-triazin in acetone were then added to the beaker.

After stirring the bath gently for five minutes, a 2.5 M NaOH-solution was added drop-wise while continuing to stir the bath. A total of 30 ml NaOH-solution were added over a period of fifteen minutes. The bath was then stirred gently for a further thirty minutes, whereafter the liquid was removed and the fibres were washed repeatedly with 95 vol% ethanol. The fibres were then dried at room temperature.

Example 6 - Characterization of absorption properties with the aid of liquid porosymmetry

Liquid porosymmetry

A fibre network made of fibres produced in accordance with the invention was characterized with the aid of a PVD-apparatus (Pore Volume Distribution) manufactured by Textile Research Institute, Princeton, U.S.A. The function of the PVD-apparatus is described concisely in Miller, B. and Tyomkin, L., Text. Res. J. 56 (1986) 35 and described briefly below, referring to Fig. 9.

Liquid was applied to the sample (in this case 0.9% NaCL-solution and so-called synthetic urine, respectively) in an excess amount and the sample allowed to absorb the liquid over a given period (in this case 5 h). The sample 13 was then placed in a chamber 14 on a membrane 15, and a porous plate 16, a mechanical load (in this case 2.5 kPa) in the form of a lead weight being placed on top. The chamber was then sealed-off and the chamber air pressure increased progressively in stages with the aid of a computer-controlled pressurizing system, the liquid being exited from the

sample through a small-pore membrane (in this case a pore size of 0.22 μm). The weight of the liquid pressed from the sample was recorded by a balance scale 17.

According to Laplace equation [1], a given pressure corresponds to a given pore radius.

$$\Delta P = \frac{2\gamma Cos\theta}{r} \qquad [1]$$

where

ΔP = The pressure necessary for pressing-out liquid hydraulically.

γ = The surface tension of the liquid.

θ = Contact angle between liquid and examined material.

r = Pore radius.

When surface tension and contact angle are constant, the pressure increase is thus reciprocally proportional to the pore radius.

This gives a relationship between pressure difference and liquid volume, which can be described schematically in accordance with the Figure 7 diagram.

When this cumulative relationship is derivated, there is obtained a pore volume distribution as shown diagrammatically in Figure 8. The distribution function reveals the amount of liquid retained by pores of a given size.

In this work, liquid contained in pores greater than 3 mm has been defined as capillary liquid, and liquid in pores smaller than 3 mm as gel liquid. The capillary

liquid is found in pores between the fibres, whereas the gel liquid is found in the interior of the fibres and in pores on the surfaces thereof.

According to the Laplace equation [1], the pressure required to remove the gel liquid is greater than the pressure required to remove the capillary-bound liquid. It can be said therefore that the gel liquid is "firmly" bound to the material, whereas the capillary liquid is bound less firmly.

A comparison between so-called superabsorbents and pulp fibres shows that the difference in gel-liquid content is very great when the liquid is comprised of water, 0.9% NaCl-solution, so-called synthetic urine or some other substance that swells superabsorbents.

The liquid porosymmetry method thus provides good possibilities of examining the ability of the material to retain firmly-bound liquid, and a distribution function which describes how the capillary, less firmly-bound, liquid is retained in the material.

Figure 9 is a schematic illustration of the construction of the PVD-apparatus.

Fibres from Example 1, spun in a bath containing 3 g $AlCl_3 \cdot 6H_2O$/l 95 vol% ethanol and 5 vol% water, and fibres from Example 5 were characterized with the aid of the PVD-apparatus described above. Sample bodies were formed from the aforesaid fibres. So-called synthetic urine was used as test liquid and the materials were loaded with a pressure of 2.5 kPa during the measuring process.

The following materials were also tested for comparison purposes:

1. CTMP (Mölnlycke)
2. Sulphate pulp (Korsnäs)
3. Superabsorbent powder, Sanwet® IM 2200D (Hoechst)

Result

Table 1 shows the values obtained with regard to gel liquid, capillary bound liquid and the total amount of liquid absorbed.

Table 1

Sample	Gel liquid g/g	Capillary liquid g/g	Total liquid g/g	
CTMP	1.37	8.78	10.75	
Sulphate pulp	0.86	6.24	7.10	
Sanwet® IM 2200D		16.85	16.12	32.97
CMC-fibres Example 1	19.90	10.00	29.90	
CMC-fibres Example 5	14.40	16.85	31.25	

The ability of Sanwet® IM 200D and CMC-fibres to absorb gel liquid was found to be several times greater than the ability of the pulp fibres. A comparison between the CMC-fibres from Example 1 and Example 5 shows that the covalently cross-linked fibres from Example 5 have a greater ability to take-up capillary-bound liquid.

Figures 10 and 11 illustrate the pore volume distribution of the materials tested. It will be seen from Figure 11 that the fibre network comprised of covalently cross-linked CMC-fibres has larger pores than the fibres which are not covalently cross-linked. This should be advantageous from the aspect of flow resistance when liquid shall be transported between the fibres in an absorbent article. The pore structure of the commercial polyacrylate superabsorbent Sanwet® IM 2200D is equivalent to the pore structure of the covalently cross-linked CMC-fibre from Example 5.

Example 7 - The swelling capacity of the fibres

Free swelling capacity is defined as the swelling capacity of a material that is not subjected to pressure.

Figure 5 illustrates the free swelling capacity of CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg. The liquids tested were 0.9% NaCl, synthetic urine and synthetic menstruation fluid. By synthetic urine and synthetic menstruation fluid is meant synthetically prepared liquids which were similar to their natural counterparts with regard to physical properties and chemical composition.

Figure 6 illustrates a comparison with regard to free-swelling between CMC-fibres produced in accordance with Example 1 from Cekol 50000 and having an aluminium content of 7.7 g/kg, and two commercially available CMC-materials, Aqualon® ACU D-3273 (Hercules) and E228-95 (Hoechst). It will be seen from the Figure that CMC-fibres produced in accordance with Example 1 have a higher free-swelling capacity than the commercially available CMC-materials.

NEW CLAIMS

1. A method of producing polysaccharide fibres, **characterized** by dissolving a polysaccharide in a solvent, and spraying the solution into a bath which contains a water-miscible organic solvent and a cross-linker.

2. A method of producing polysaccharide fibres in accordance with Claim 1, **characterized** by stretching, rolling-up, drying and cutting the polysaccharide fibres after the bath.

3. A method of producing polysaccharide fibres according to Claim 1 or Claim 2, **characterized** in that the organic solvent is an alcohol or a ketone.

4. A method of producing polysaccharide fibres according to Claim 3, **characterized** in that the organic solvent is methanol, ethanol, isopropanol or acetone.

5. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** in that the cross-linker is a polyelectrolyte.

6. A method of producing polysaccharide fibres according to Claim 5, **characterized** in that the cross-linker is polyvinylamine or Polybrene® (hexadimethrinbromide).

7. A method of producing polysaccharide fibres according to any one of Claims 1-4, **characterized** in that the cross-linker is a salt where the cation in the salt is a metal ion.

8. A method of producing polysaccharide fibres according to Claim 7, **characterized** in that the cation in the salt is divalent, trivalent or quadrivalent.

9. A method of producing polysaccharide fibres according to Claim 8, **characterized** in that the cation in the salt is calcium, magnesium, iron, aluminium or zirconium.

10. A method of producing polysaccharide fibres according to any one of Claims 7-9, **characterized** in that the anion in the metal salt is chloride.

11. A method of producing polysaccharide fibres according to any one of the preceding Claims, **characterized** in that the polysaccharide is comprised of carboxymethyl cellulose, starch, cellulose xanthane, gelan, chitin, chitosan, guar gum or alginate.

12. A method of producing polysaccharide fibres in accordance with any one of the preceding Claims, **characterized** by cross-linking the fibre covalently in a following stage.

13. A polysaccharide fibre, **characterized** by having been produced in accordance with any one of the preceding Claims.

14. A polysaccharide fibre according to claim 13, **characterized** in that the fibre has been solvent-spun and has a degree of substitution greater than 0.35, is cross-linked, and insoluble, but swellable, in water.

15. An absorbent structure in an absorbent article, such as a diaper, an incontinence guard or a sanitary napkin, characterized in that the absorbent structure includes polysaccharide fibres having been produced in accordance with any one of Claims 1-12.

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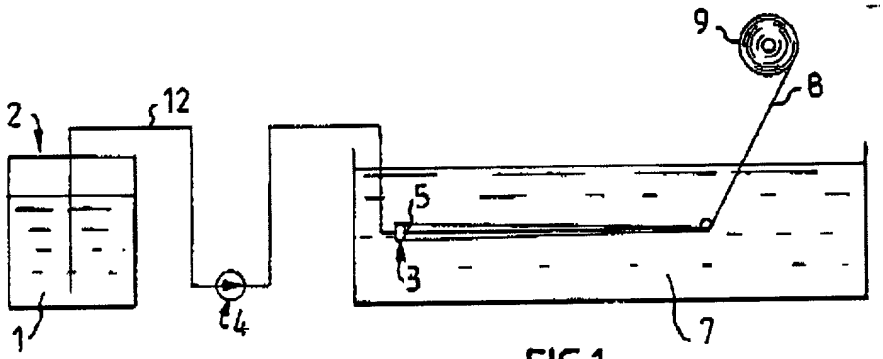

FIG.1

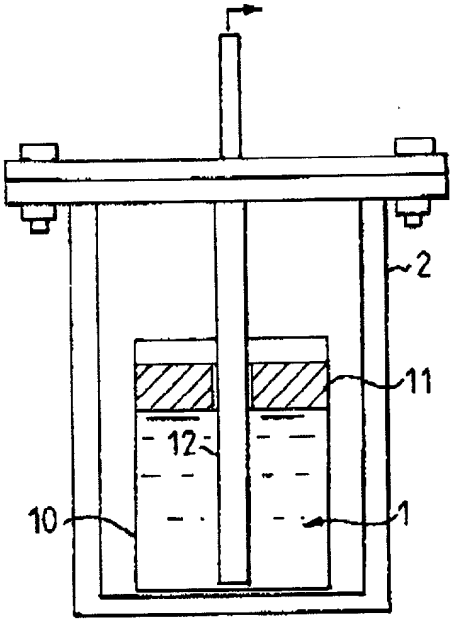

FIG. 2

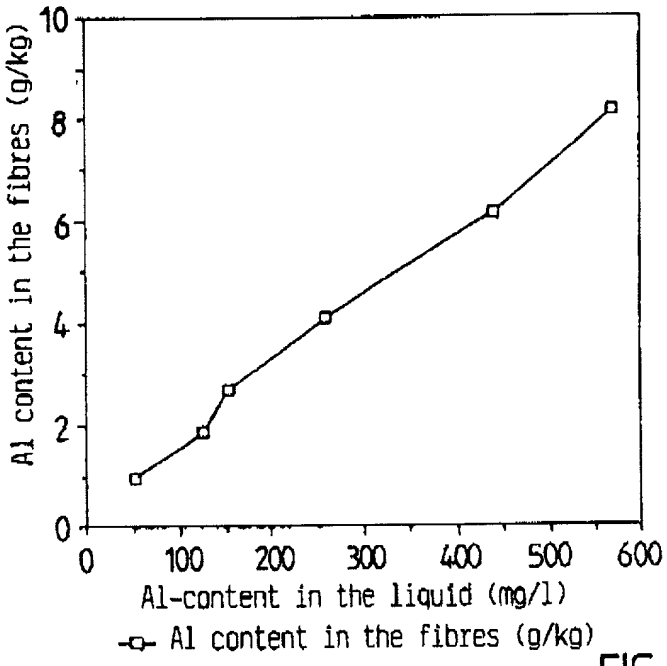
Al content in the fibres (g/kg)
0
2
4
6
8
10
0
100
200
300
400
500
600
Al-content in the liquid (mg/l)
Al content in the fibres (g/kg)

FIG. 3

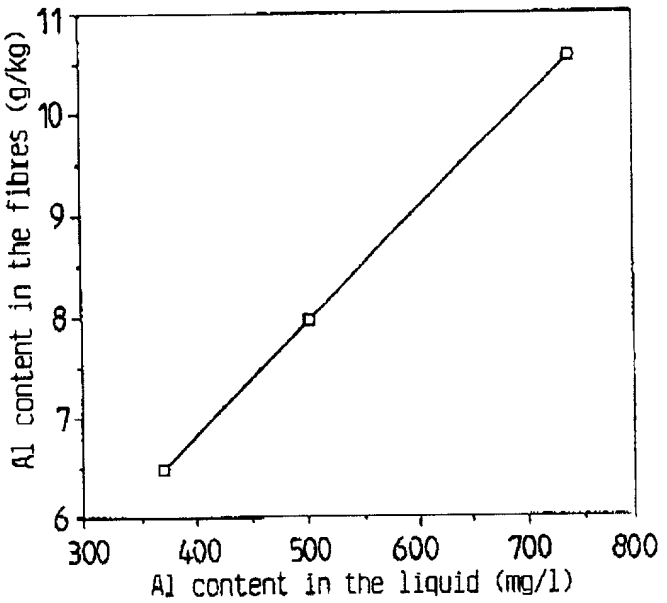
Al content in the fibres (g/kg)
6
7
8
9
10
11
300
400
500
600
700
800
Al content in the liquid (mg/l)
Al content in the fibres (g/kg)

FIG. 4

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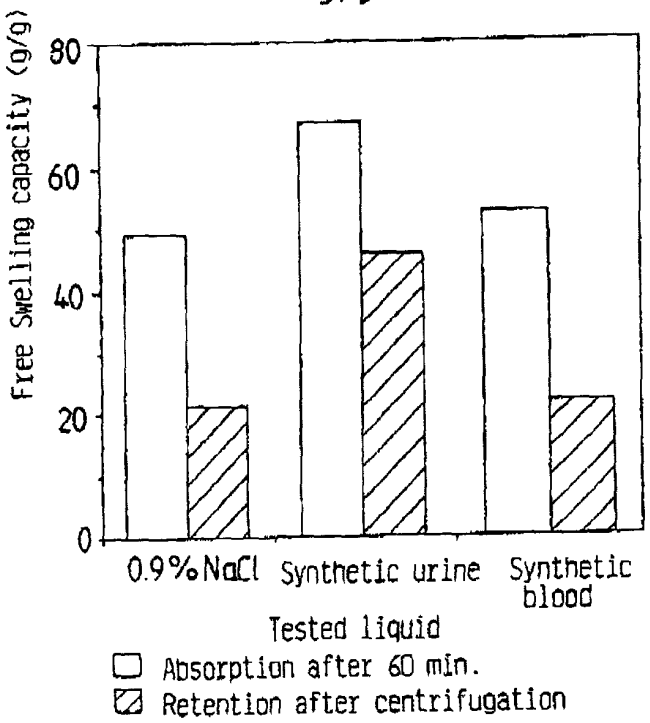

FIG. 5

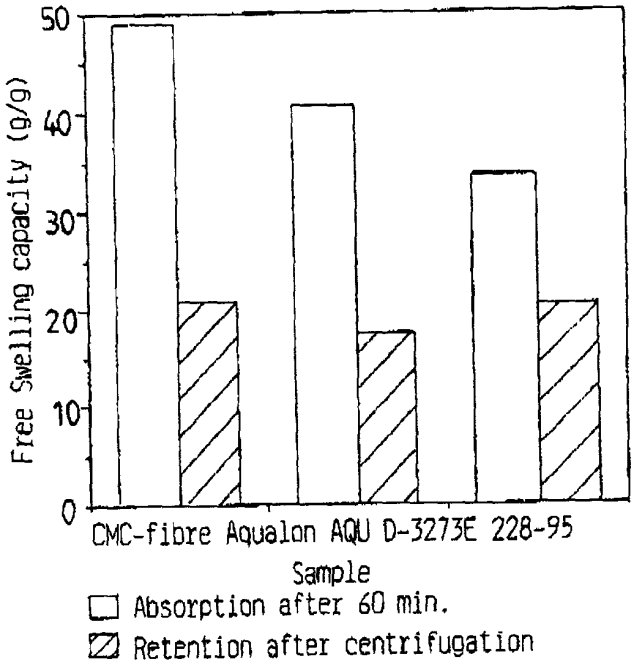

FIG.6

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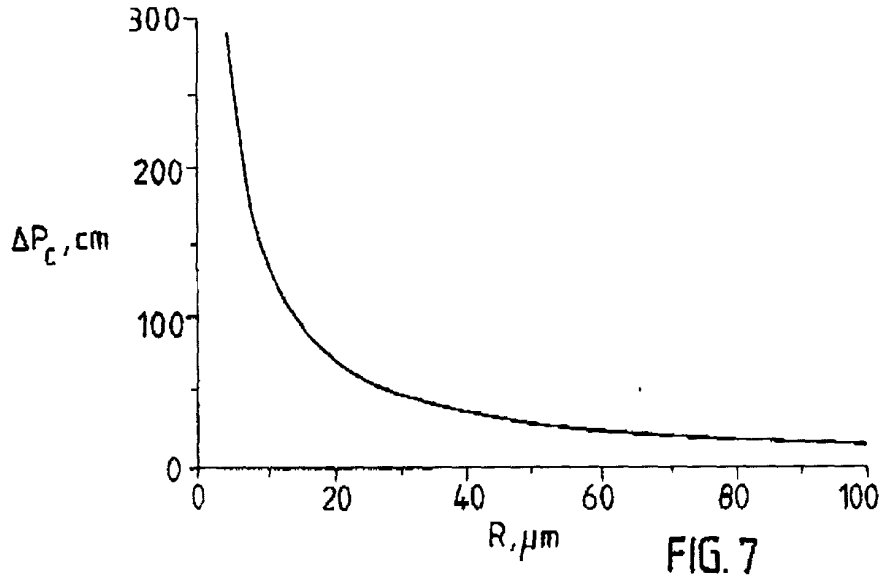

FIG. 7

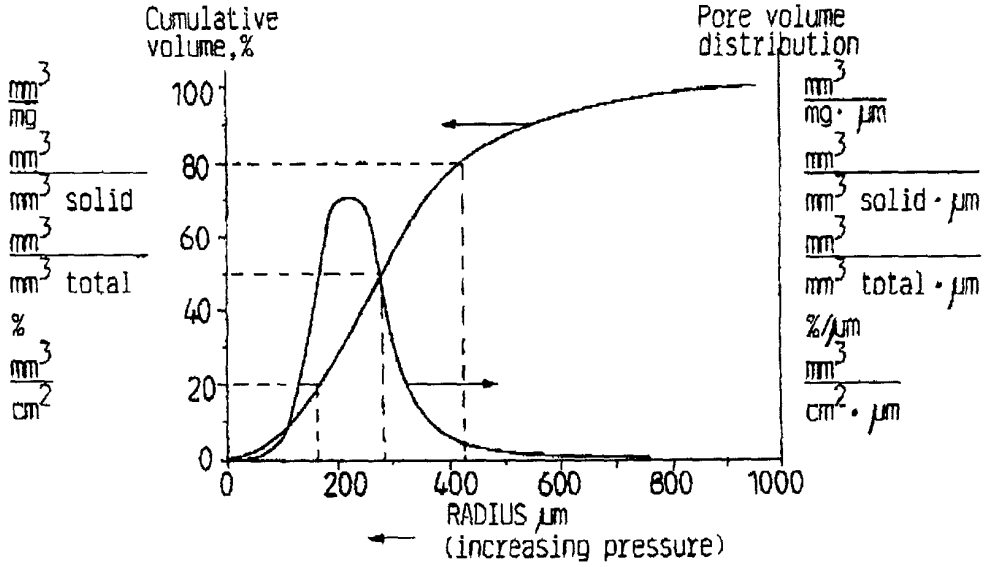

FIG. 8

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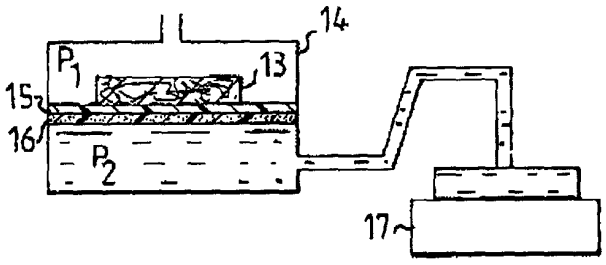

FIG.9

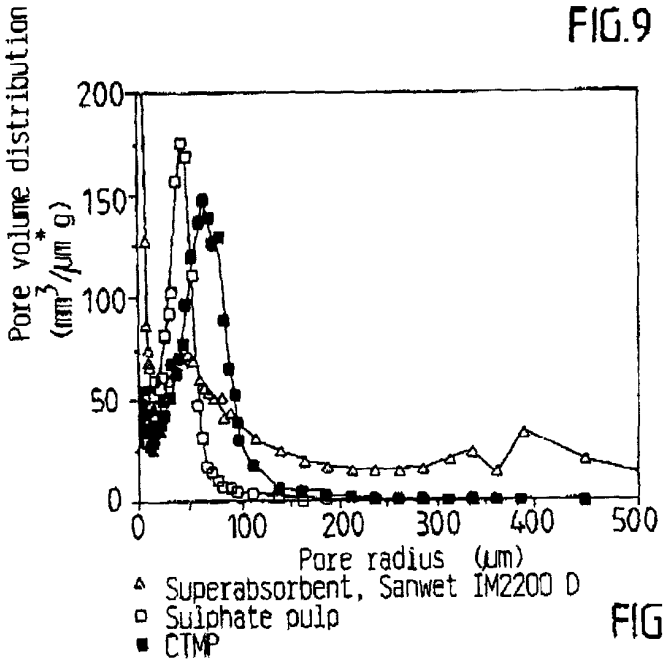

FIG.10

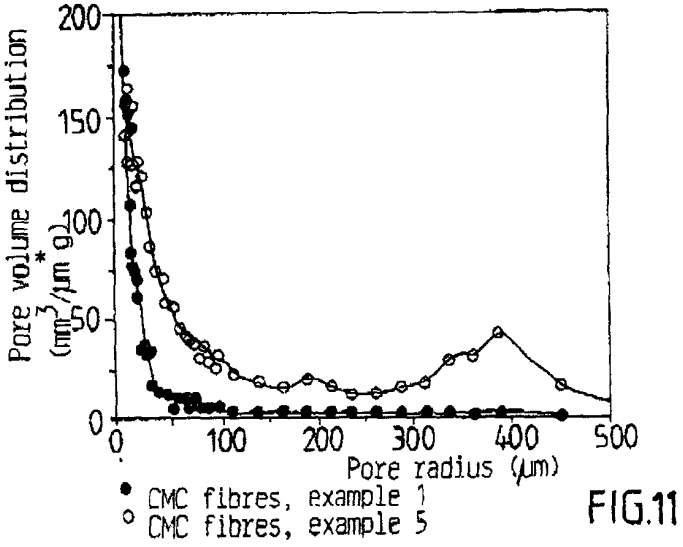

FIG.11

COMBINED DECLARATION AND POWER OF ATTORNEY FOR UTILITY PATENT APPLICATION	Attorney Docket No.

As a below named inventor, I hereby declare that:
My residence, post office address and citizenship are as stated below next to my name;
I BELIEVE I AM THE ORIGINAL, FIRST AND SOLE INVENTOR (if only one name is listed below) OR AN ORIGINAL, FIRST AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION

ENTITLED: A method of producing an absorbent material, an absorbent material and absorbent articles including the material in question.

the specification of which:

(check one) ☐ is attached hereto;
☒ was filed on 18 December 1996 as

Application Serial No. PCT/SE96/01698

and was amended on _____; (if applicable)

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE;

I ACKNOWLEDGE THE DUTY TO DISCLOSE INFORMATION WHICH IS MATERIAL TO THE EXAMINATION OF THIS APPLICATION IN ACCORDANCE WITH TITLE 37, CODE OF FEDERAL REGULATIONS, Sec. 1.56 (a) which states: "A duty of candor and good faith toward the Patent and Trademark Office rests on the inventor, on each attorney or agent who prepares or prosecutes the application and on every other individual who is associated with the inventor, with the assignee or with anyone to whom there is an obligation to assign the application. All such individuals have a duty to disclose to the Office information they are aware of which is material to the examination of the application. Such information is material where there is a substantial likelihood that a reasonable examiner would consider it important in deciding whether to allow the application to issue as a patent. The duty is commensurate with the degree of involvement in the preparation or prosecution of the application.";

I do not know and do not believe the said invention was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to said application; that said invention was not in public use or on sale in the United States of America more than one year prior to said application; that said invention has not been patented or made the subject of an inventor's certificate issued before the date of said application in any country foreign to the United States of America on any application filed by me or my legal representatives or assigns more than twelve months prior to said application;

I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application(s) on which priority is claimed:

COMBINED DECLARATION AND POWER OF ATTORNEY

Attorney Docket No.

COUNTRY/INTERNATIONAL	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
Sweden	9600087-2	10.01.96	YES X NO
			YES NO

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

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Platon N. Mandros	22,124	Alan E. Kopecki	25,813	L. Joseph Gess	28,510
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Joel M. Freed	25,101	Ralph L. Freeland, Jr.	16,110		

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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FULL NAME OF THIRD JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		

☐ Please see attached continuation page for additional inventors.